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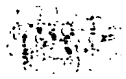

Patents Form 1/77

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1/77

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road
Newport
Gwent NP9 1RH

1. Your reference

99C102 RCS

2. Patent application number
(The Patent Office will fill in this part)

06 FEB 1999

9902592.6

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

Hoechst Schering AgrEvo GmbH
Miraustr. 54
D-13509 Berlin
Germany

Patents ADP number *(if you know it)*

If the applicant is a corporate body, give the country/state of its incorporation

Germany 6696462001

4. Title of the invention

Fungicides

5. Name of your agent *(if you have one)*

R C Sewell

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

AgrEvo UK Limited
Patent Department
Chesterford Park
Saffron Walden
Essex CB10 1XL

6501200001

Patents ADP number *(if you know it)*

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

Yes

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	
Description	32
Claim(s)	4
Abstract	
Drawing(s)	

10. If you are also filing any of the following, state how many against each item.

Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature [signature] Date 5.2.99

12. Name and daytime telephone number of person to contact in the United Kingdom Dr R C Sewell - 01799 573342

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Notes

a) If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.

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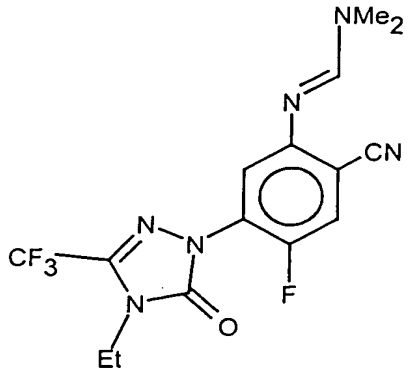
Fungicides

This invention relates to the use of compounds as fungicides.

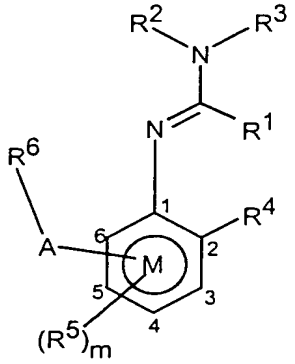
WO 95/22532 relates to substituted phenyltriazolinones claimed as herbicides and discloses *inter alia* a compound of formula A for which there is no characterising data therein.



(A)

The abstract, composition claim and use claim refer only to the use of such compounds as herbicides and indeed the description supports the invention only with herbicidal activity data. There is a sentence in the specification that states that certain compounds show fungicidal activity, although no fungicidal activity data is provided. No indication is given as to which compounds are fungicidal and there is no suggestion that compound A could be fungicidal.

We have now found that certain amidines have fungicidal activity. Therefore, the invention provides the use of a compound of general formula I and salts thereof as fungicides



(I)

wherein

R^1 is alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl, each of which may be substituted, or hydrogen;

R^2 and R^3, which may be the same or different, are any group defined for R^1; cyano; acyl; $-OR^a$ or $-SR^a$, where R^a is alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl, each of which may be substituted; or R^2 and R^3, or R^2 and R^1, together with their interconnecting atoms may form a ring, which may be substituted;

R^4 is alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl, each of which may be substituted; hydroxy; mercapto; azido; nitro; halogen; cyano; acyl; optionally substituted amino; cyanato; thiocyanato; $-SF_5$; $-OR^a$; $-SR^a$ or $-Si(R^a)_3$;

m is 0 to 3;

when present R^5, which may be the same or different to any other R^5, is any group defined for R^4;

R^6 is optionally substituted carbo- or heterocyclyl; and

A is a direct bond, $-O-$, $-S(O)_n-$, $-NR^9-$, $-CR^7=CR^7-$, $-C\equiv C-$, $-A^1-$, $-A^1-A^1-$, $-A^3-$, $-A^4-$, $-A^1O-$, $-A^1S(O)_n-$, $-OA^1-$, $-S(O)_nA^1-$, $-A^1-A^4-$, $-A^1-A^4-C(R^8)=N-N=CR^8-$, $-A^1-A^4-C(R^8)=N-X^2-X^3-$, $-A^1-A^4-A^3-$, $-A^1-A^4-N(R^9)-$, $-A^1-A^4-X-CH_2-$, $-A^1-A^4-A^1-$, $-A^1-A^4-CH_2X-$, $-A^1-A^4-C(R^8)=N-X^2-X^3-X^1-$, $-A^1-X-C(R^8)=N-$, $-A^1-X-C(R^8)=N-N=CR^8-$, $-A^1-X-C(R^8)=N-N(R^9)-$, $-A^1-X-A^-X^1-$, $-A^1-O-A^3-$, $-A^1-O-C(R^7)=C(R^8)-$, $-A^1-O-N(R^9)-A^2-N(R^9)-$, $-A^1-O-N(R^9)-A^2-$, $-A^1-N(R^9)-A^2-N(R^9)-$, $-A^1-N(R^9)-A^2-$, $-A^1-N(R^9)-N=C(R^8)-$, $-A^3-A^1-$, $-A^4-A^3-$, $-A^2-NR^9-$, $-A^1-A^2-X^1-$, $-A^1-A^1-A^2-X^1-$, $-O-A^2-N(R^9)-A^2-$, $-CR^7=CR^7-A^2-X^1-$, $-C\equiv C-A^2-X^1-$, $-N=C(R^8)-A^2-X^1-$, $-C(R^8)=N-N=C(R^8)-$, $-C(R^8)=N-N(R^9)-$, $-(CH_2)_2-O-N=C(R^8)-$ or $-X-A^2-N(R^9)-$

where

n is 0, 1 or 2,

A^1 is $-CHR^7-$,

A^2 is $-C(=X)-$,

A^3 is $-C(R^8)=N-O-$,

A^4 is $-O-N=C(R^8)-$,

X is O or S;

X^1 is O, S, NR^9 or a direct bond,

X^2 is O, NR^9 or a direct bond,

X^3 is hydrogen, $-C(=O)-$, $-SO_2-$ or a direct bond,

R^7, which may be the same or different to any other R^7, is optionally substituted alkyl, cycloalkyl or phenyl, each of which may be optionally substituted, hydrogen, halogen or cyano;

R^8, which may be the same or different to any other R^8, is alkyl, alkenyl, alkynyl, alkoxy, alkylthio, each of which may be optionally substituted, carbo- or heterocyclyl which may be optionally substituted, or hydrogen;

R^9, which may be the same or different to any other R^9, is optionally substituted alkyl, optionally substituted carbo- or heterocyclyl, or is hydrogen or acyl; or two R^9 groups on A, together with the connecting atoms, form a 5 to 7 membered ring;

where the moiety depicted on the right side of linkage A is attached to R^6;

or $-A-R^6$ and R^5 together with benzene ring M form an optionally substituted fused ring system.

Preferably R^1 is alkyl, alkenyl or alkynyl, each of which may be substituted by alkoxy, haloalkoxy, alkylthio, halogen or optionally substituted phenyl; or is hydrogen. R^1 is especially C_1-C_5 alkyl or hydrogen.

Preferably R^2 and R^3, each of which may be the same or different, are alkyl, alkenyl or alkynyl, which may be substituted by alkoxy, haloalkoxy, alkylthio, halogen or optionally substituted phenyl; or is hydrogen. R^2 and R^3, which may be the same or different, are especially C_1-C_5 alkyl or hydrogen.

Preferably R^4 is alkyl, alkenyl, or alkynyl, each of which may be substituted by alkoxy, haloalkoxy, alkylthio, halogen or optionally substituted phenyl; hydroxy;

halogen; cyano; acyl; alkoxy; haloalkoxy; or alkylthio. R^4 is especially C_1-C_5 alkyl or halogen.

Preferably m is 0 or 1.

When present, R^5 is preferably alkyl, alkenyl, or alkynyl, each of which may be substituted by alkoxy, haloalkoxy, alkylthio, halogen or optionally substituted phenyl; hydroxy; halogen; cyano; acyl; alkoxy; haloalkoxy; or alkylthio. R^5 is especially C_1-C_5 alkyl.

When present, the group R^5 is preferably attached at the 5 position of ring M.

Preferably A is a direct bond; –O-; -S-; -NR^9-, -CHR^7- or -O-CHR^7-. R^9 is alkyl, alkenyl, or alkynyl, each of which may be substituted by alkoxy, haloalkoxy, alkylthio, halogen or optionally substituted phenyl; or is hydrogen (especially C_1-C_5 alkyl or hydrogen). R^7 is alkyl, alkenyl, or alkynyl, each of which may be substituted by alkoxy, haloalkoxy, alkylthio, halogen or optionally substituted phenyl; hydroxy; halogen; cyano; acyl; alkoxy; haloalkoxy; alkylthio; or hydrogen (especially C_1-C_5 alkyl or hydrogen)

Preferably A is attached to the 4 position of benzene ring M.

Most compounds of general formula I are novel. Therefore according to a second aspect, the invention provides compounds of formula I wherein

R^1 is alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl, each of which may be substituted, or hydrogen;

R^2 and R^3, which may be the same or different, are any group defined for R^1, or together with the nitrogen to which they are attached may form a ring, which may be substituted;

R^4 is alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl, each of which may be substituted;

m is 1;

R^5 is any group defined for R^4 attached to the 5-position of the benzene ring M;

R^6 is optionally substituted carbo- or heterocyclyl; and

A is a direct bond; –O-; -S-; $-NR^9-$, where R^9 is alkyl, alkenyl, or alkynyl, each of which may be substituted by alkoxy, haloalkoxy, alkylthio, halogen or optionally substituted phenyl; $-CHR^7-$ or $-O-CHR^7-$, where R^7 is alkyl, alkenyl, or alkynyl, which may be substituted by alkoxy, haloalkoxy, alkylthio, halogen or optionally substituted phenyl; hydroxy; halogen; cyano; acyl; alkoxy; haloalkoxy; or alkylthio;

where $-A-R^6$ is in the 4-position of the benzene ring M and the moiety depicted on the right side of linkage A is attached to R^6;

or $-A-R^6$ and R^5 together with benzene ring M form an optionally substituted fused ring system.

Any alkyl group may be straight or branched and is preferably of 1 to 10 carbon atoms, especially 1 to 7 and particularly 1 to 5 carbon atoms.

Any alkenyl or alkynyl group may be straight or branched and is preferably of 2 to 7 carbon atoms and may contain up to 3 double or triple bonds which may be conjugated, for example vinyl, allyl, butadienyl or propargyl.

Any carbocyclyl group may be saturated, unsaturated or aromatic, and contain 3 to 8 ring-atoms. Preferred saturated carbocyclyl groups are cyclopropyl, cyclopentyl or cyclohexyl. Preferred unsaturated carbocyclyl groups contain up to 3 double bonds. A preferred aromatic carbocyclyl group is phenyl. The term carbocylic should be similarly construed. In addition, the term carbocyclyl includes any fused combination of carbocyclyl groups, for example naphthyl, phenanthryl, indanyl and indenyl.

Any heterocyclyl group may be saturated, unsaturated or aromatic, and contain 5 to 7 ring-atoms up to 4 of which may be hetero-atoms such as nitrogen, oxygen and sulfur. Examples of heterocyclyl groups are furyl, thienyl, pyrrolyl, pyrrolinyl, pyrrolidinyl, imidazolyl, dioxolanyl, oxazolyl, thiazolyl, imidazolyl, imidazolinyl, imidazolidinyl, pyrazolyl, pyrazolinyl, pyrazolidinyl, isoxazolyl, isothiazolyl, oxadiazolyl, triazolyl, thiadiazolyl, pyranyl, pyridyl, piperidinyl, dioxanyl,

morpholino, dithianyl, thiomorpholino, pyridazinyl, pyrimidinyl, pyrazinyl, piperazinyl, sulfolanyl, tetrazolyl, triazinyl, azepinyl, oxazepinyl, thiazepinyl, diazepinyl and thiazolinyl. In addition, the term heterocyclyl includes fused heterocyclyl groups, for example benzimidazolyl, benzoxazolyl, imidazopyridinyl, benzoxazinyl, benzothiazinyl, oxazolopyridinyl, benzofuranyl, quinolinyl, quinazolinyl, quinoxalinyl, dihydroquinazolinyl, benzothiazolyl, phthalimido, benzofuranyl, benzodiazepinyl, indolyl and isoindolyl. The term heterocyclic should be similarly construed.

Any alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl group, when substituted, may be substituted by one or more substituents, which may be the same or different, and may be selected from the list: hydroxy; mercapto; azido; nitro; halogen; cyano; acyl; optionally substituted amino; optionally substituted carbocyclyl; optionally substituted heterocyclyl; cyanato; thiocyanato; $-SF_5$; $-OR^a$; $-SR^a$ and $-Si(R^a)_3$, where R^a is alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl, each of which may be substituted. In the case of any carbocyclyl or heterocyclyl group the list includes additionally: alkyl, alkenyl and alkynyl, each of which may be substituted. Preferred substituents on any alkyl, alkenyl or alkynyl group are alkoxy, haloalkoxy or alkylthio, each containing 1 to 5 carbon atoms; halogen; or optionally substituted phenyl. Preferred substituents on any carbocyclyl or heterocyclyl group are alkyl, haloalkyl, alkoxy, haloalkoxy or alkylthio, each containing 1 to 5 carbon atoms; halogen; or optionally substituted phenyl.

In the case of any alkyl group or any unsaturated ring-carbon in any carbocyclyl or heterocyclyl group the list includes a divalent group such as oxo or imino, which may be substituted by optionally substituted amino, R^a or $-OR^a$ (where R^a is as defined above). Preferred groups are oxo, imino, alkylimino, oximino, alkyloximino or hydrazono.

Any amino group, when substituted and where appropriate, may be substituted by one or two substituents which may be the same or different, selected from the list: optionally substituted alkyl, optionally substituted amino, $-OR^a$ (where R^a is as defined above) and acyl groups. Alternatively two substituents together with the nitrogen to which they are attached may form a heterocyclyl group, preferably

a 5 to 7-membered heterocyclyl group, which may be substituted and may contain other hetero atoms, for example morpholino, thiomorpholino or piperidinyl.

The term acyl includes the residues of sulfur and phosphorus-containing acids as well as carboxylic acids. Typically the residues are covered by the general formulae $-C(=X^a)R^b$, $-S(O)_pR^b$ and $-P(=X^a)(OR^a)(OR^a)$, where appropriate X^a is O or S, R^b is as defined for R^a, $-OR^a$, $-SR^a$, optionally substituted amino or acyl; and p is 1 or 2. Preferred groups are $-C(=O)R^c$, $-C(=S)R^c$,and $-S(O)_pR^c$ where R^c is alkyl, C_1 to C_5 alkoxy, C_1 to C_5 alkylthio, phenyl, heterocyclyl or amino, each of which may be substituted.

Complexes of compounds of the invention are usually formed from a salt of formula MAn_2, in which M is a divalent metal cation, e.g. copper, manganese, cobalt, nickel, iron or zinc and An is an anion, e.g. chloride, nitrate or sulfate.

In cases where the compounds of the invention exist as the E and Z isomers, the invention includes individual isomers as well as mixtures thereof.

In cases where compounds of the invention exist as tautomeric isomers, the invention includes individual tautomers as well as mixtures thereof.

In cases where the compounds of the invention exist as optical isomers, the invention includes individual isomers as well as mixtures thereof.

The compounds of the invention have activity as fungicides, especially against fungal diseases of plants, e.g. mildews and particularly cereal powdery mildew (*Erysiphe graminis*) and vine downy mildew (*Plasmopara viticola*), rice blast (*Pyricularia oryzae*), cereal eyespot (*Pseudocercosporella herpotrichoides*), rice sheath blight (*Pellicularia sasakii*), grey mould (*Botrytis cinerea*), damping off (*Rhizoctonia solani*), wheat brown rust (*Puccinia recondita*), late tomato or potato blight (*Phytophthora infestans*), apple scab (*Venturia inaequalis*), and glume blotch (*Leptosphaeria nodorum*). Other fungi against which the compounds may be active include other powdery mildews, other rusts, and other general

pathogens of Deuteromycete, Ascomycete, Phycomycete and Basidomycete origin.

The invention thus also provides a method of combating fungi at a locus infested or liable to be infested therewith, which comprises applying to the locus a compound of formula I.

The invention also provides an agricultural composition comprising a compound of formula I in admixture with an agriculturally acceptable diluent or carrier.

The composition of the invention may of course include more than one compound of the invention.

In addition, the composition can comprise one or more additional active ingredients, for example compounds known to possess plant-growth regulant, herbicidal, fungicidal, insecticidal, acaricidal, antimicrobial or antibacterial properties. Alternatively the compound of the invention can be used in sequence with the other active ingredient.

The diluent or carrier in the composition of the invention can be a solid or a liquid optionally in association with a surface-active agent, for example a dispersing agent, emulsifying agent or wetting agent. Suitable surface-active agents include anionic compounds such as a carboxylate, for example a metal carboxylate of a long chain fatty acid; an *N*-acylsarcosinate; mono- or di-esters of phosphoric acid with fatty alcohol ethoxylates or alkyl phenol ethoxylates or salts of such esters; fatty alcohol sulfates such as sodium dodecyl sulfate, sodium octadecyl sulfate or sodium cetyl sulfate; ethoxylated fatty alcohol sulfates; ethoxylated alkylphenol sulfates; lignin sulfonates; petroleum sulfonates; alkyl-aryl sulfonates such as alkyl-benzene sulfonates or lower alkylnaphthalene sulfonates, e.g. butyl-naphthalene sulfonate; salts of sulfonated naphthalene-formaldehyde condensates; salts of sulfonated phenol-formaldehyde condensates; or more complex sulfonates such as the amide sulfonates, e.g. the sulfonated condensation product of oleic acid and *N*-methyl taurine; the dialkyl sulfosuccinates, e.g. the sodium sulfonate of dioctyl succinate; acid derivatives of alkyl glycosides and alkylpolyglycosides materials and their metal salts, e.g. alkyl

polyglycoside citrate or tartrate materials; or mono-, di- and tri-alkyl esters of citric acid and their metal salts.

Nonionic agents include condensation products of fatty acid esters, fatty alcohols, fatty acid amides or fatty-alkyl- or alkenyl-substituted phenols with ethylene and/or propylene oxide; fatty esters of polyhydric alcohol ethers, e.g. sorbitan fatty acid esters; condensation products of such esters with ethylene oxide, e.g. polyoxyethylene sorbitan fatty acid esters; alkyl glycosides, alkyl polyglycoside materials; block copolymers of ethylene oxide and propylene oxide; acetylenic glycols such as 2,4,7,9-tetramethyl-5-decyne-4,7-diol, ethoxylated acetylenic glycols; acrylic based graft copolymers; alkoxylated siloxane surfactants; or imidazoline type surfactants, e.g. 1-hydroxyethyl-2-alkylimidazoline.

Examples of a cationic surface-active agent include, for instance, an aliphatic mono-, di-, or polyamine as an acetate, naphthenate or oleate; an oxygen-containing amine such as an amine oxide, polyoxyethylene alkylamine or polyoxypropylene alkylamine; an amide-linked amine prepared by the condensation of a carboxylic acid with a di- or polyamine; or a quaternary ammonium salt.

The compositions of the invention can take any form known in the art for the formulation of agrochemicals, for example, a solution, an aerosol, a dispersion, an aqueous emulsion, a microemulsion, a dispersible concentrate, a dusting powder, a seed dressing, a fumigant, a smoke, a dispersible powder, an emulsifiable concentrate, granules or an impregnated strip. Moreover it can be in a suitable form for direct application or as a concentrate or primary composition which requires dilution with a suitable quantity of water or other diluent before application.

A dispersible concentrate comprises a compound of the invention dissolved in one or more water miscible or semi-water miscible solvents together with one or more surface activeand/or polymeric material. Addition of the formulation to water results in the crystalisation of the active ingredient, the process being controlled by the surfactants and/or polymers resulting in a fine dispersion.

A dusting powder comprises a compound of the invention intimately mixed and ground with a solid pulverulent diluent, for example, kaolin.

An emulsifiable concentrate comprises a compound of the invention dissolved in a water-immiscible solvent which forms an emulsion or microemulsion on addition to water in the presence of an emulsifying agent.

A granular solid comprises a compound of the invention associated with similar diluents to those that may be employed in dusting powders, but the mixture is granulated by known methods. Alternatively it comprises the active ingredient absorbed or coated on a pre-formed granular carrier, for example, Fuller's earth, attapulgite, silica or limestone grit.

Wettable powders, granules or grains usually comprise the active ingredient in admixture with suitable surfactants and an inert powder diluent such as clay or diatomaceous earth.

Another suitable concentrate is a flowable suspension concentrate which is formed by grinding the compound with water or other liquid, surfactants and a suspending agent.

The concentration of the active ingredient in the composition of the present invention, as applied to plants is preferably within the range of 0.0001 to 1.0 per cent by weight, especially 0.0001 to 0.01 per cent by weight. In a primary composition, the amount of active ingredient can vary widely and can be, for example, from 5 to 95 per cent by weight of the composition.

In use a compound of the invention is generally applied to seeds, plants or their habitat. Thus, the compound can be applied directly to the soil before, at or after drilling so that the presence of active compound in the soil can control the growth of fungi which may attack seeds. When the soil is treated directly the active compound can be applied in any manner which allows it to be intimately mixed with the soil such as by spraying, by broadcasting a solid form of granules, or by applying the active ingredient at the same time as drilling by inserting it in the

same drill as the seeds. A suitable application rate is within the range of from 5 to 1000 g per hectare, more preferably from 10 to 500 g per hectare.

Alternatively the active compound can be applied directly to the plant by, for example, spraying or dusting either at the time when the fungus has begun to appear on the plant or before the appearance of fungus as a protective measure. In both such cases the preferred mode of application is by foliar spraying. It is generally important to obtain good control of fungi in the early stages of plant growth, as this is the time when the plant can be most severely damaged. The spray or dust can conveniently contain a pre- or post-emergence herbicide if this is thought necessary. Sometimes, it is practicable to treat the roots, bulbs, tubers or other vegetative propagule of a plant before or during planting, for example, by dipping the roots in a suitable liquid or solid composition. When the active compound is applied directly to the plant a suitable rate of application is from 0.025 to 5 kg per hectare, preferably from 0.05 to 1 kg per hectare.

In addition, the compounds of the invention can be applied to harvested fruits, vegetables or seeds to prevent infection during storage.

In addition, the compounds of the invention can be applied to plants or parts thereof which have been genetically modified to exhibit a trait such as fungal and/or herbicidal resistance.

In addition the compounds of the invention can be used to treat fungal infestations in timber and in public health applications. Also the compounds of the invention can be used to treat fungal infestations in domestic and farm animals.

Compounds of the invention may be prepared, in known manner, in a variety of ways.

Compounds of general formula I may be prepared from compounds of general formula II according to Scheme 1. The following reaction conditions may be used to effect conversion:

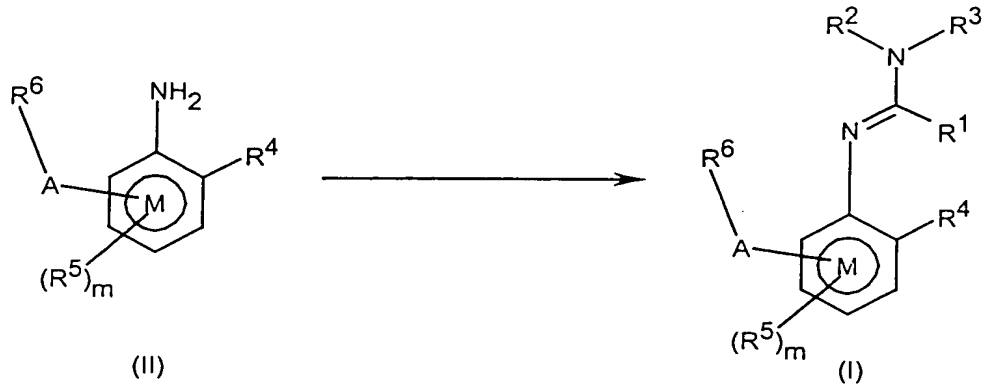
a) reaction with $R^2R^3NC(R^1)(OR)_2$, where R is a group such as alkyl;

b) reaction with $ROC(R^1)=NCN$;

c) when R^1 is hydrogen, by reaction with $H(C=O)NR^2R^3$ in the presence of $POCl_3$ or $SOCl_2$; or

d) in two steps by reaction with phosgene to form the isocyanate and then treatment with $R^2R^3N(C=O)R^1$.

Scheme 1



(II) (I)

In addition, groups R^2 and R^3 in compounds of general formula I can be converted to other groups defined for R^2 and R^3, by treatment with an appropriate amine.

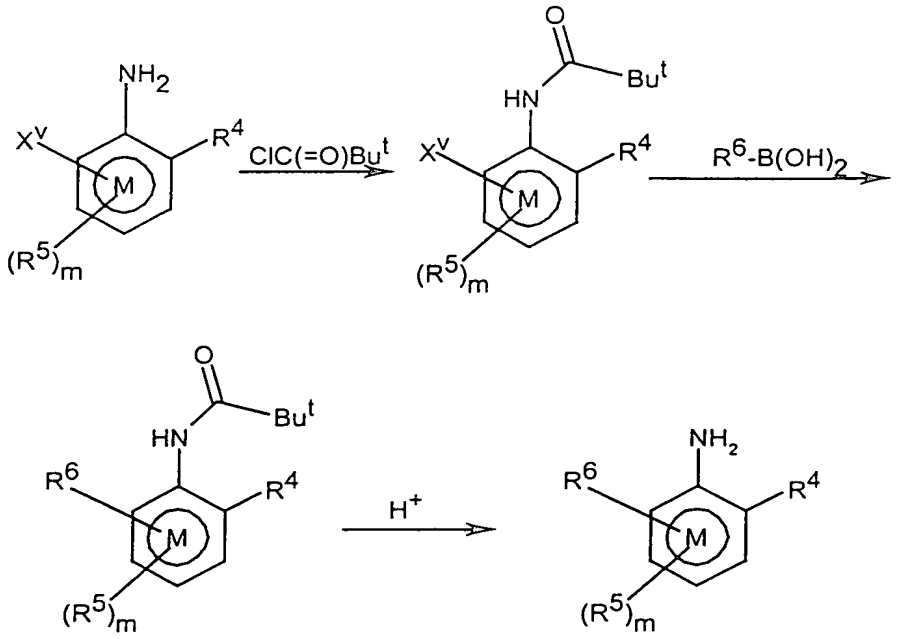
Compounds of general formula II may be prepared by reduction of the nitro group in compounds of formula III according to reaction scheme 2. Preferred reaction conditions comprise reaction with stannous chloride in concentrated hydrochloric acid.

Scheme 2

(III) (II)

Compounds of formula IIa, i.e. compounds of general formula II where A is a direct bond, may be prepared according to reaction scheme 3, where X^v is a leaving group.

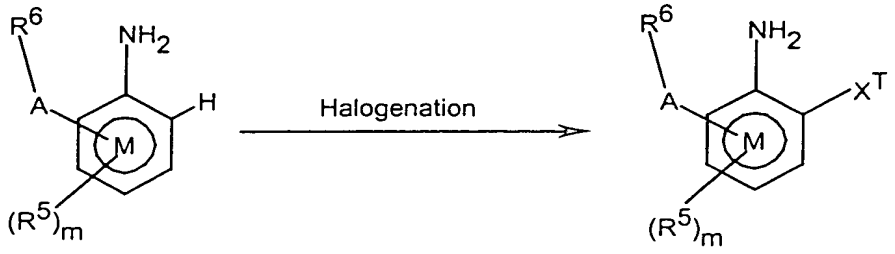
Scheme 3



(IIa)

Compounds of formula IIb, i.e. compounds of general formula II where R^4 is halogen, may be prepared according to scheme 4, where X^T is halogen. When X^T is bromine preferred reaction conditions comprise stirring with bromine in a suitable solvent.

Scheme 4

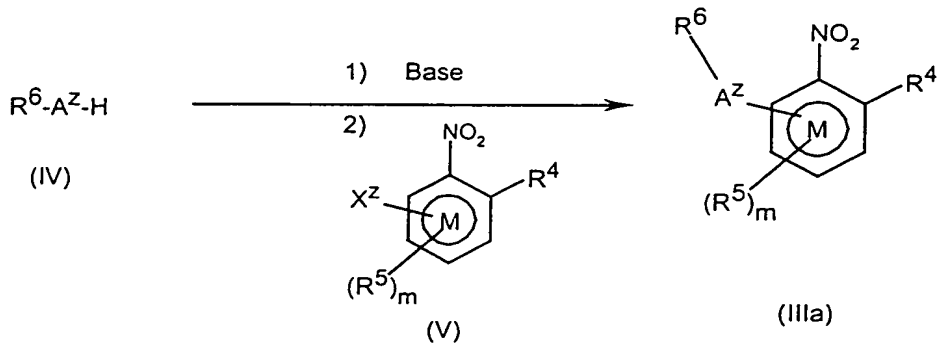


(IIb)

Compounds of formula IIIa, i.e. compounds of general formula III where A is a group A^z, may be prepared by reacting compounds of formula IV with compounds of formula V according to reaction scheme 5. A^z is a group which, in compound IV, forms an anion under basic conditions. X^z is a leaving group, preferably

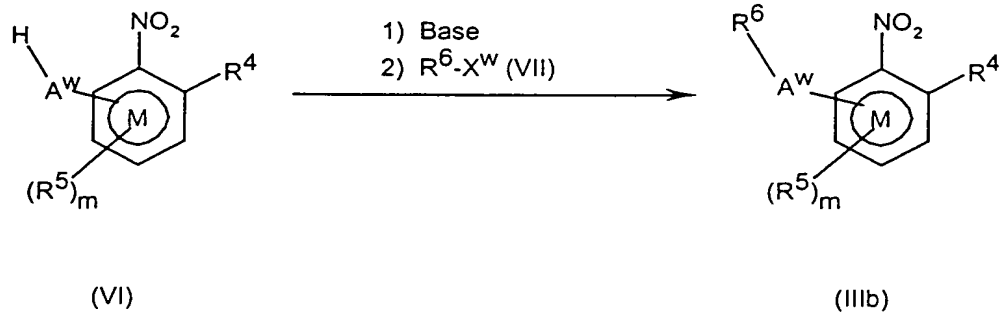
halogen. When A^z is oxygen, preferred reaction conditions comprise treating IV with sodium hydride followed by addition of V. When A^z is sulfur preferred reaction conditions comprise reacting IV with V in the presence of a tertiary amine base such as ethyldiisopropylamine.

Scheme 5



Compounds of formula IIIb, i.e. compounds of general formula III where A is a group A^W, may be prepared by reacting compounds of formula VI with compounds of formula VII according to reaction scheme 6. A^W is a group which, in compound VI, forms an anion under basic conditions. X^W is a leaving group, preferably halogen. Preferred basic conditions comprise reaction of VI with potassium carbonate or sodium hydride followed by addition of VII.

Scheme 6

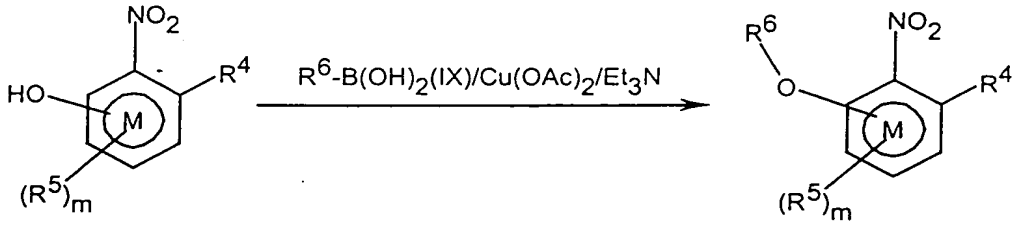


(VI) (IIIb)

Compounds of formula IIIc, i.e. compounds of general formula III where A is O, may be prepared by reacting compounds of formula VIII with boronic acids of

formula IX according to Scheme 7. Preferred reaction conditions comprise reaction with copper acetate and triethylamine.

Scheme 7

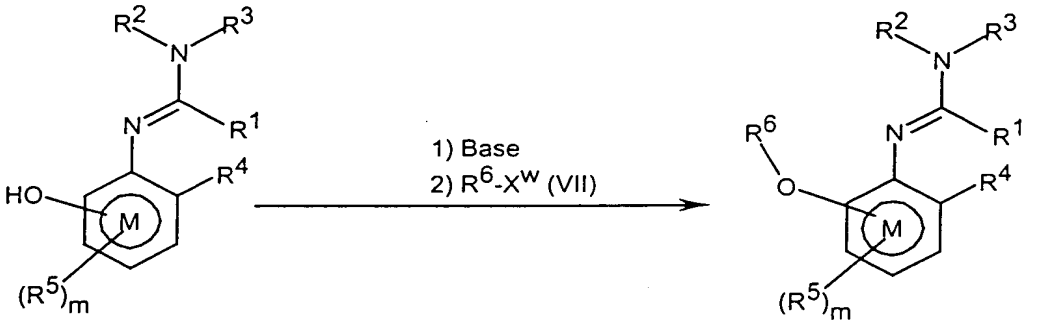


(VIII) (IIIc)

Alternatively, using similar chemistry to that described above, compounds of formula I can be prepared by introducing R^6 after formation of the amidine moiety.

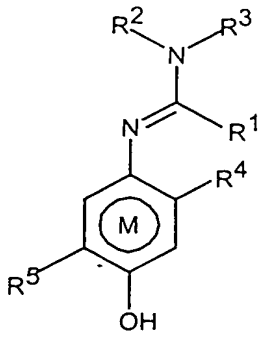
In particular, we have found that treating compounds of formula IX to the reaction conditions of Scheme 6 gives compounds of formula Ia, i.e. compounds of general formula I where A is oxygen, in particularly high yield (see Scheme 8). Compounds of formula IX may be prepared by methods similar to those described in *Tetrahedron Letters*, 38 (31) 5403-5406.

Scheme 8



(IX) (Ia)

Some compounds of general formula IX are novel, therefore according to a third aspect the invention provides compounds of general formula IXa,



(IXa)

where

R^1 is alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl, each of which may be substituted, or hydrogen;

R^2 and R^3, which may be the same or different, are any group defined for R^1; cyano; acyl; $-OR^a$ or $-SR^a$, where R^a is alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl, each of which may be substituted; or R^2 and R^3, or R^2 and R^1, together with their interconnecting atoms may form a ring, which may be substituted;

R^4 is alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl, each of which may be substituted; and

R^5 is any group defined for R^4;

with the proviso that R^5 is not tert-butyl.

Other methods will be apparent to the chemist skilled in the art, as will be methods for preparing starting materials and intermediates.

In addition, compounds of the invention may be prepared using combinatorial chemistry methodology.

The invention is illustrated in the following Examples. Structures of isolated, novel compounds were confirmed by NMR and/or other appropriate analyses.

Example 1

N,N-Dimethyl-*N'*-[4-(3-trifluoromethylbenzylthio)-2,5-xylyl]formamidine (Compound 3)

The product from stage b) (1.0 g) and *N,N*-dimethylformamide dimethylacetal (1.0 ml) were heated at 100 °C for 4 hours. On cooling the mixture was purified by silica gel chromatography eluting with diethyl ether to give the title compound, ^{1}H N.M.R. δ(ppm) 2.15 (s, 3H, Ar$\underline{CH_3}$), 2.20 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 6H, N($\underline{CH_3}$)$_2$), 3.95 (s, 2H, S$\underline{CH_2}$).

Preparation of Starting Materials

a) 2-Nitro-5-(3-trifluoromethylbenzylthio)-*p*-xylene

A mixture of 3-trifluoromethylbenzyl mercaptan (3.42 g), diisopropylethylamine (2.3 g) and 3-chloro-6-nitro-*p*-xylene (3.0 g) in dry *N*-methylpyrrolidinone (20 ml) was heated at 130 °C for 6 hours. On cooling, the mixture was poured into ice water and the resulting mixture was filtered to give a solid which was washed with ice-water and the air dried. The solid was purified by silica gel chromatography eluting with light petroleum (60-80°C)/ethyl acetate (9:1) to give the title product as a solid, m.p. 85-7°C.

b) 4-(3-Trifluoromethylbenzylthio)-2,5-xylidine

To a stirred mixture of stannous chloride (10.8 g) in concentrated hydrochloric acid (24 ml) and ethanol (50 ml) was added the product from stage a) above (2.46 g) and the mixture was heated at 75 °C for 2 hours. On cooling potassium hydroxide solution was added slowly with cooling. The mixture was extracted with diethyl ether (x3) and the combined extracts were washed with brine, dried ($MgSO_4$), filtered and evaporated to dryness to give a crude residue which was purified by silica gel chromatography eluting with light petroleum (b.p.60-80 °C)/ethyl acetate (3:1) to give the title product, m.p. 58-60 °C.

Example 2

N,N-Diethyl-*N'*-[4-(3-trifluoromethylphenoxy)-2,5-xylyl]formamidine (Compound 37)

Under an atmosphere of nitrogen, phosphous oxychloride (2.18 g) in dry diethyl ether (3 ml) was added dropwise to a stirred solution of *N,N*-diethylformamide (1.43 g) in dry diethyl ether (3 ml) and stirring continued for 20 minutes. Stirring was stopped and the mixture allowed to form two layers. The upper ether layer was removed by decanting, and the lower layer was washed with diethyl ether (x3). The product from stage b) (2 g) in dry diethyl ether (4 ml) was then added dropwise. After addition the mixture was stirred vigorously for 1 hour at room temperature. The upper ether layer was removed by decanting and the lower layer was washed with ether (x2). The lower layer was poured into water and the mixture adjusted to pH 9 with sodium carbonate solution. The mixture was extracted with diethyl ether (x3) and the combined extracts were dried ($MgSO_4$), filtered and evaporated to dryness to give a crude oil which was purified by silica gel chromatography eluting with diethyl ether to give the title compound, ^1H N.M.R. δ(ppm) 1.20 (t, 6H, $CH_2\underline{CH_3}$), 2.10 (s, 3H, $Ar\underline{CH_3}$), 2.20 (s, 3H, $Ar\underline{CH_3}$), 3.30-3.50 (br, 4H, $\underline{CH_2}CH_3$).

Preparation of Starting materials

a) 2-Nitro-5-(3-trifluoromethylphenoxy)-*p*-xylene

To a suspension of sodium hydride (0.4 g of 60% in oil) in dry *N*-methylpyrrolidinone (10 ml) was slowly added 3-trifluoromethylphenol (1.62 g). When effervescence had ceased, 3-chloro-6-nitro-*p*-xylene (1.85 g) was added and the mixture stirred at 120-40 °C for 5 hours. On cooling, the mixture was poured into water and the mixture extracted with diethyl ether (x3). The combined ether extracts were dried ($MgSO_4$), filtered and evaporated to give the title compound as a solid, m.p. 68-71 °C.

b) 4-(3-Trifluoromethylphenoxy)-2,5-xylidine

This compound was prepared in similar fashion to the product from Example 1, stage b).

Example 3

N-Ethyl-*N*-methyl-*N'*-[4-(3-trifluoromethylphenoxy)-2,5-xylyl]formamidine (Compound 45)

A mixture of the product from Example 4 (1 g) and methylethylamine (0.885 g) in acetonitrile (20 ml) was stirred at room temperature for 1.5 hours. The solvent was removed *in vacuo* and water added. The mixture was extracted with diethyl ether (x3) and the combined ether extracts dried ($MgSO_4$), filtered and evaporated to dryness. The crude residue was purified by silica gel chromatography eluting with ethyl acetate/light petroleum (b.p. 40-60 °C) (4:6) to give the title compound, ^1H N.M.R. δ(ppm) 1.20 (t, 3H, $CH_2\underline{CH_3}$), 2.10 (s, 3H, $Ar\underline{CH_3}$), 2.20 (s, 3H, $Ar\underline{CH_3}$), 3.00 (s, 3H, $N\underline{CH_3}$), 3.40 (br, 2H, $N\underline{CH_2}$).

Example 4

N-Cyano-*N'*-[4-(3-trifluoromethylphenoxy)-2,5-xylyl]formamidine (Compound 44)

To a solution of starting material from Example 2 (2 g) in ethanol (5 ml) was added dropwise ethyl cyanoimidate (0.7 g) at room temperature and stirring continued for 2 hours at room temperature. The ethanol was removed *in vacuo* to give a crude residue which was purified by trituration with light petroleum (b.p. 40-60 °C) followed by silica gel chromatography eluting with ethyl acetate/light petroleum (b.p. 40-60 °C) (4:6) to give the title product, m.p. 138-40 °C.

Example 5

N,N-Dimethyl-*N'*-[4-(3-phenyl-1,2,4-thiadiazol-5-yloxy)-2,5-xylyl]formamidine (Compound 48)

To a suspension of the starting material (see below) (0.57 g) in dimethylformamide (10 ml) was added potassium carbonate (0.62 g) and the solution stirred at room temperature for 40 minutes. 5-Bromo-3-phenyl-1,2,4-thiadiazole (0.72 g) was added and the mixture stirred at 60 °C for 3 hours. On cooling the mixture was poured into water (150 ml) and extracted with diethyl ether (3x70 ml). The combined ether extracts were washed with water (20 ml), dried ($MgSO_4$), filtered and evaporated to dryness to give a crude solid which was purified by silica gel chromatography eluting with diethyl ether to give the title compound as a solid, m.p. 100-5 °C.

Preparation of Starting Materials

N,N-Dimethyl-*N'*-(4-hydroxy-2,5-xylyl)formamidine

This compound was prepared from 4-amino-2,5-dimethylphenol in similar fashion to Examples 1, 2 or 3, m.p. 212 °C.

Example 6

N,N-Dimethyl-*N'*-[4-(3-trifluoromethylphenoxy)-2,6-xylyl]formamidine (Compound 20)

This compound was prepared from the product of stage b) below and dimethylformamide dimethylacetal according to the method of Example 1, ^{1}H N.M.R. δ(ppm) 2.15 (s, 6H, Ar$\underline{CH_3}$), 3.00 (s, 6H, N($\underline{CH_3}$)$_2$).

Preparation of starting materials

a) 2-Nitro-5-(3-trifluoromethylphenoxy)-*m*-xylene

A mixture of 3,5-dimethyl-4-nitrophenol (1.67 g), 3-trifluoromethylbenzene boronic acid (3.8 g), copper (II) acetate (1.82 g) and triethylamine (2.02 g) in dichloromethane (50 ml) was stirred at room temperature for 48 hours. The mixture was evaporated to dryness and purified by silica gel chromatography eluting with light petroleum (b.p. 60-80 °C)/ethyl acetate (19:1) to give the title product as an oil.

b) 4-(3-Trifluoromethylphenoxy)-2,6-xylidine

This compound was prepared from the product of stage a) above according to the method of Example 1, stage b).

Example 7

N,N-Dimethyl-*N'*-[6-bromo-4-(3-trifluoromethylphenoxy)-2,5-xylyl]formamidine (Compound 12)

The title product was prepared from the product of stage c) below and dimethylformamide dimethylacetal according to Example 1, ^{1}H N.M.R. δ(ppm) 2.17 (s, 3H, Ar$\underline{CH_3}$), 2.22 (s, 3H, Ar$\underline{CH_3}$), 3.05 (s, 6H, N($\underline{CH_3}$)$_2$).

Preparation of Starting Materials

a) 2-Nitro-5-(3-trifluoromethylphenoxy)-*p*-xylene

The title product was prepared from 2,5-dimethyl-4-nitrophenol and 3-trifluoromethylbenzene boronic acid according to Example 6, stage a).

b) 4-(3-Trifluoromethylphenoxy)-2,5-xylidine

The title product was prepared from the product of stage a) according to Example 1, stage b).

c) 6-Bromo-4-(3-trifluoromethylphenoxy)-2,5-xylidine

To a stirred solution of the product from stage b) above (1.12 g) in dichloromethane (20 ml) was added dropwise bromine (0.64 g) in dichloromethane (5 ml) at 0 °C. The mixture was washed with sodium bicarbonate solution, dried ($MgSO_4$), filtered and evaporated to give a crude oil which was purified by silica gel chromatography eluting with ethyl acetate/ light petroleum (b.p. 60-80 °C) (1:4) to give the title product.

Example 8

N,N-Dimethyl-*N'*-[4-(3-trifluoromethylphenyl)-2,5-xylyl]formamidine (Compound 53)

The title product was prepared from the product of stage c) below and dimethylformamide dimethylacetal according to Example 1, ^{1}H N.M.R. δ(ppm) 2.00 (s, 3H, Ar$\underline{CH_3}$), 2.20 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 6H, (N$\underline{CH_3}$)$_2$).

Preparation of Starting Materials

a) *N*-(4-Bromo-2,5-xylyl)pivalamide

To a solution of 4-bromo-2,5-xylidine (8 g) in pyridine (60 ml) was added pivaloyl chloride (4.7 ml) at room temperature. After 30 minutes, the mixture was poured into dilute hydrochloric acid/ice solution. The precipitate was filtered and washed with water to give the title product.

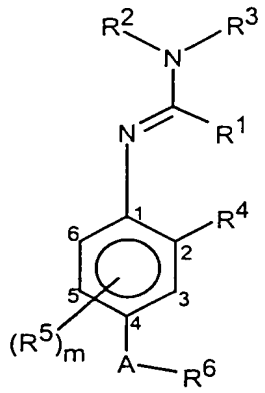
b) *N*-(4-(3-Trifluoromethylphenyl)-2,5-xylyl)pivalamide

To a solution of the product of stage a) (9.1 g) in dimethoxyethane (14 ml) was added triphenylphosphinepaladium (II) chloride (a spatular-tip full) and stirred for 10 minutes. 3-Trifluoromethyphenylboronic acid (6.03 g), sodium bicarbonate (8.1 g) and water (102 ml) were added and the mixture heated under relfux for 4 hours. On cooling 1N sodium hydroxide solution (94 ml) was added the mixture extracted with ethyl acetate. The organic extracts were washed with stauarate sodium chloride solution, dried ($MgSO_4$) and concentrated to give the title product.

c) 4-(3-Trifluoromethylphenyl)-2,5-xylidine

The product from stage b) (10.4 g) in glacial acetic acid (36 ml) was treated with hydrochloric acid (24.5 ml of 15% solution) at 70 °C. The mixture was stirred for 3 days at 100 °C. On cooling, water was added and the mixture extracted with ethyl acetate. The organic phase was washed with sodium bicarbonate solution, dried ($MgSO_4$) and concentrated to give the title product.

The following compounds of formula Ia (see Table 1), i.e. compounds of general formula I where $-A-R^6$ is para to the amidine moiety, may be prepared by methods analogous to those of Examples 1 to 8. Where the moiety depicted on the right side of linkage A is attached to R^6;



(Ia)

Table 1

Cmp	R^1	R^2	R^3	R^4	$(R^5)_m$	A	R^6	m.p./°C
1	H	Me	Me	Me	5-Me	O	3-CF_3-phenyl	49-50
2	Me	Me	Me	Me	5-Me	O	3-CF_3-phenyl	oil
3	H	Me	Me	Me	5-Me	SCH_2	3-CF_3-phenyl	oil
4	H	Me	Me	Me	5-Me	S	3-CF_3-phenyl	oil
5	Me	Me	Me	Me	5-Me	SCH_2	3-CF_3-phenyl	oil
6	Me	Me	Me	Me	5-Me	S	3-CF_3-phenyl	oil
7	H	Me	Me	Me	5-Me	O	3-Cl-phenyl	oil
8	H	Me	Me	Me	5-Me	O	3-Bu^t-phenyl	69-71
9	H	Me	Me	Me	5-Me	O	4-tolyl	oil
10	Me	Me	Me	Me	5-Me	OCH_2	3-CF_3-phenyl	oil
11	H	Me	Me	Me	5-Me	OCH_2	3-CF_3-phenyl	50-4
12	H	Me	Me	Me	5-Me,6-Br	O	3-CF_3-phenyl	oil
13	H	Me	Me	Me	-	O	3-CF_3-phenyl	oil
14	H	Me	Me	CF_3	-	O	3-CF_3-phenyl	oil
15	H	Me	Me	Br	5-OMe	O	3-CF_3-phenyl	68-70
16	H	Me	Me	Me	5-Me	-OCH(Me)-	3-CF_3-phenyl	97-9
17	H	Me	Me	Me	5-Me	OCH_2	3-PhO-phenyl	oil
18	H	Me	Me	Br	5-Me,6-Br	O	3-CF_3-phenyl	oil
19	H	Me	Me	Br	5-Me	O	3-CF_3-phenyl	oil
20	H	Me	Me	Me	6-Me	O	3-CF_3-phenyl	oil
21	H	Me	Me	Me	5-Pr^i	O	3-CF_3-phenyl	oil
22	H	Me	Me	Me	5-Me	O	2-biphenylyl	oil
23	H	Me	Me	Me	5-Me	O	3-F-phenyl	oil
24	H	Me	Me	Me	5-Me	O	4-CF_3-phenyl	oil
25	H	Me	Me	Me	5-Me	O	2-CF_3-phenyl	oil
26	H	Me	Me	Me	5-Me	O	3,4-diMeO-phenyl	oil
27	H	Me	Me	Me	5-Me	O	2-MeO-phenyl	oil
28	H	Me	Me	Me	5-Me	O	3-PhO-phenyl	oil
29	H	Me	Me	Me	5-Me	O	3-CN-phenyl	oil
30	H	Me	Me	Me	5-Me	O	benzoxazol-2-yl	107-9
31	H	Me	Me	Me	5-Me	O	2,6-xylyl	oil

Cmp	R^1	R^2	R^3	R^4	$(R^5)_m$	A	R^6	m.p./°C
32	H	Me	Me	Me	5-Me	O	3,4-diCl-phenyl	oil
33	H	Me	Me	Me	5-Me	O	3-EtOC(=O)-phenyl	oil
34	H	Me	Me	Me	5-Me	O	4-tolyl	oil
35	H	$-(CH_2)_2O(CH_2)_2-$		Me	5-Me	O	3-CF_3-phenyl	oil
36	H	Me	Me	Me	5-Me	O	3-CF_3-phenyl	122-3
37	H	Et	Et	Me	5-Me	O	3-CF_3-phenyl	oil
38	H	Pr	Pr	Me	5-Me	O	3-CF_3-phenyl	oil
39	H	Bu	Bu	Me	5-Me	O	3-CF_3-phenyl	oil
40	H	Pr^i	Pr^i	Me	5-Me	O	3-CF_3-phenyl	oil
41	H	$-(CH_2)_4-$		Me	5-Me	O	3-CF_3-phenyl	71-3
42	H	Ph	Me	Me	5-Me	O	3-CF_3-phenyl	oil
43	H	$-(CH_2)_5-$		Me	5-Me	O	3-CF_3-phenyl	oil
44	H	H	CN	Me	5-Me	O	3-CF_3-phenyl	138-40
45	H	Et	Me	Me	5-Me	O	3-CF_3-phenyl	oil
46	H	Pr	H	Me	5-Me	O	3-CF_3-phenyl	44-6
47	H	benzyl	H	Me	5-Me	O	3-CF_3-phenyl	121-3
48	H	Me	Me	Me	5-Me	O	3-Ph-1,2,4-thiadiazol-5-yl	100-5
49	H	Me	Me	Me	5-Me	-OCH(Me)-	3-CF_3-phenyl	97-9
50	H	Me	Me	Me	5-Me	O	4-CF_3-phenyl	oil
51	H	Me	Me	Me	5-Me	O	2-CF_3-phenyl	oil
52	H	Me	Me	Me	5-Me	O	3-Cl-5-CF_3-2-pyridyl	oil
53	H	Me	Me	Me	5-Me	direct bond	3-CF_3-phenyl	oil
54	H	Me	Me	Me	5-Me	O	benzoxazol-2-yl	107-9

Those compounds in table 1 which do not have discrete melting points have the following characteristic ^1H N.M.R. data in $CDCl_3$.

Compound 2

^1H N.M.R. δ(ppm) 1.78 (s, 3H, N=C$\underline{CH_3}$), 2.00 (s, 3H, Ar$\underline{CH_3}$), 2.18 (s, 3H, Ar$\underline{CH_3}$), 3.05 (s, 6H, N($C\underline{H_3}$)$_2$)

Compound 3

^{1}H N.M.R. δ(ppm) 2.15 (s, 3H, Ar$\underline{CH_3}$), 2.20 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 6H, N($\underline{CH_3}$)$_2$), 3.95 (s, 2H, S$\underline{CH_2}$)

Compound 4

^{1}H N.M.R. δ(ppm) 2.00 (s, 3H, Ar$\underline{CH_3}$), 2.20 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 6H, N($\underline{CH_3}$)$_2$)

Compound 5

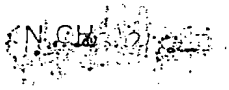
^{1}H N.M.R. δ(ppm) 1.70 (s, 3H, N=C$\underline{CH_3}$), 1.90 (s, 3H, Ar$\underline{CH_3}$), 2.10 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 6H, N($\underline{CH_3}$)$_2$), 3.90 (s, 2H, S$\underline{CH_2}$)

Compound 6

^{1}H N.M.R. δ(ppm) 1.80 (s, 3H, N=C$\underline{CH_3}$), 2.00 (s 3H, Ar$\underline{CH_3}$), 2.20 (s, 6H, N($\underline{CH_3}$)$_2$), 3.00 (s, 6H, N($\underline{CH_3}$)$_2$)

Compound 7

^{1}H N.M.R. δ(ppm) 2.10 (s, 3H, Ar$\underline{CH_3}$), 2.20 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 6H,



Compound 9

^{1}H N.M.R. δ(ppm) 2.10 (s, 3H, Ar$\underline{CH_3}$), 2.20 (s, 3H, Ar$\underline{CH_3}$), 2.30 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 6H, N($\underline{CH_3}$)$_2$)

Compound 10

^{1}H N.M.R. δ(ppm) 1.75 (s, 3H, N=C$\underline{CH_3}$), 2.00 (s, 3H, Ar$\underline{CH_3}$), 2.20 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 6H, N($\underline{CH_3}$)$_2$), 5.10 (s, 2H, Ar$\underline{CH_2}$

Compound 12

^{1}H N.M.R. δ(ppm) 2.17 (s, 3H, Ar$\underline{CH_3}$), 2.22 (s, 3H, Ar$\underline{CH_3}$), 3.05 (s, 6H, N($\underline{CH_3}$)$_2$)

Compound 13

^{1}H N.M.R. δ(ppm) 2.25 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 6H, N($\underline{CH_3}$)$_2$)

Compound 14

^{1}H N.M.R. δ(ppm) 3.00 (s, 6H, N(CH_3)$_2$)

Compound 17

^{1}H N.M.R. δ(ppm) 2.18 (s, 3H, Ar$\underline{CH_3}$), 2.22 (s, 3H, Ar$\underline{CH_3}$), 2.99 (s, 6H, N($\underline{CH_3}$)$_2$), 5.00 (s, 2H, Ar$\underline{CH_2}$)

Compound 18

^{1}H N.M.R. δ(ppm) 2.20 (s, 3H, Ar$\underline{CH_3}$), 3.00 (bs, 6H, N($\underline{CH_3}$)$_2$)

Compound 19

^{1}H N.M.R. δ(ppm) 2.10 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 6H, N($\underline{CH_3}$)$_2$)

Compound 20

^{1}H N.M.R. δ(ppm) 2.15 (s, 6H, Ar$\underline{CH_3}$), 3.00 (s, 6H, N($\underline{CH_3}$)$_2$)

Compound 21

^{1}H N.M.R. δ(ppm) 1.15 (d, 6H, CH($\underline{CH_3}$)$_2$), 2.20 (s, 3H, Ar$\underline{CH_3}$), 3.00 (m, 7H, $\underline{CH}$ and N($\underline{CH_3}$)$_2$)

Compound 22

^{1}H N.M.R. δ(ppm) 2.15 (s, 3H, Ar$\underline{CH_3}$), 2.22 (s, 3H, Ar$\underline{CH_3}$), 3.04 (s, 6H, N($\underline{CH_3}$)$_2$)

Compound 23

^{1}H N.M.R. δ(ppm) 2.10 (s, 3H, Ar $\underline{CH_3}$), 2.22 (s, 3H, Ar$\underline{CH_3}$), 3.02 (s, 6H, N($\underline{CH_3}$)$_2$)

Compound 24

^{1}H N.M.R. δ(ppm) 2.10 (s, 3H, Ar $\underline{CH_3}$), 2.20 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 6H, N($\underline{CH_3}$)$_2$)

Compound 25

^{1}H N.M.R. δ(ppm) 2.10 (s, 3H, Ar $\underline{CH_3}$), 2.20 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 6H, N($\underline{CH_3}$)$_2$)

Compound 26

^{1}H N.M.R. δ(ppm) 2.14 (s, 3H, Ar$\underline{CH_3}$), 2.19 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 6H, N($\underline{CH_3}$)$_2$, 3.82 (s, 3H, O$\underline{CH_3}$), 3.96 (s, 3H, O$\underline{CH_3}$)

Compound 27

^{1}H N.M.R. δ(ppm) 2.14 (s, 3H, Ar$\underline{CH_3}$), 2.18 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 6H, N($\underline{CH_3}$)$_2$), 3.93 (s, 3H, O$\underline{CH_3}$)

Compound 28

^{1}H N.M.R. δ(ppm) 2.13 (s, 3H, Ar$\underline{CH_3}$), 2.19 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 6H, N($\underline{CH_3}$)$_2$)

Compound 29

^{1}H N.M.R. δ(ppm) 2.08 (s, 3H, Ar$\underline{CH_3}$), 2.22 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 6H, N($\underline{CH_3}$)$_2$)

Compound 31

^{1}H N.M.R. δ(ppm) 2.07 (s, 3H, Ar$\underline{CH_3}$), 2.11 (s, 6H, Ar$\underline{CH_3}$), 2.36 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 6H, N($\underline{CH_3}$)$_2$)

Compound 32

^{1}H N.M.R. δ(ppm) 2.08 (s, 3H, Ar$\underline{CH_3}$), 2.20 (s, 3H, Ar$\underline{CH_3}$), 3.01 (s, 6H, N($\underline{CH_3}$)$_2$)

Compound 33

^{1}H N.M.R. δ(ppm) 1.38 (t, 3H, $CH_2\underline{CH_3}$), 2.09 (s, 3H, $Ar\underline{CH_3}$), 2.20 (s, 3H, $Ar\underline{CH_3}$), 3.03 (s, 6H, $N(\underline{CH_3})_2$), 4.35 (q, 2H, $\underline{CH_2}$)

Compound 34

^{1}H N.M.R. δ(ppm) 2.12 (s, 3H, $Ar\underline{CH_3}$), 2.19 (s, 3H, $Ar\underline{CH_3}$), 2.26 (s, 3H, $Ar\underline{CH_3}$), 3.00 (s, 6H, $N(\underline{CH_3})_2$)

Compound 35

^{1}H N.M.R. δ(ppm) 2.05 (s, 3H, $Ar\underline{CH_3}$), 2.20 (s, 3H, $Ar\underline{CH_3}$), 3.45-3.55 (br, 4H, $\underline{CH_2}$), 3.75 (d, 4H, $\underline{CH_2}$)

Compound 37

^{1}H N.M.R. δ(ppm) 1.20 (t, 6H, $CH_2\underline{CH_3}$), 2.10 (s, 3H, $Ar\underline{CH_3}$), 2.20 (s, 3H, $Ar\underline{CH_3}$), 3.30-3.50 (br, 4H, $\underline{CH_2}CH_3$)

Compound 38

^{1}H N.M.R. δ(ppm) 0.95 (t, 6H, $CH_2\underline{CH_3}$), 1.70 (br, 4H, $CH_3\underline{CH_2}$), 2.10 (s, 3H, $Ar\underline{CH_3}$), 2.20 (s, 3H, $Ar\underline{CH_3}$), 3.10-3.50 (br, 4H, $N\underline{CH_2}$)

Compound 39

^{1}H N.M.R. δ(ppm) 1.00 (t, 6H, $CH_2\underline{CH_3}$), 1.35 (q, 4H, $\underline{CH_2}CH_3$), 1.60 (q, 4H, $NCH_2\underline{CH_2}$), 2.10 (s, 3H, $Ar\underline{CH_3}$), 2.20 (s, 3H, $Ar\underline{CH_3}$), 3.15-3.45 (br, 4H, $N\underline{CH_2}$)

Compound 40

^{1}H N.M.R. δ(ppm) 1.3 (d, 12H, $C\underline{CH_3}$), 2.10 (s, 3H, $Ar\underline{CH_3}$), 2.20 (s, 3H, $Ar\underline{CH_3}$), 3.6-4.9 (br, 2H, $C\underline{H}$)

Compound 42

^{1}H N.M.R. δ(ppm) 2.10 (s, 3H, Ar$\underline{CH_3}$), 2.30 (s, 3H, Ar$\underline{CH_3}$), 3.55 (s, 3H, N$\underline{CH_3}$)

Compound 43

^{1}H N.M.R. δ(ppm) 1.55-1.75 (m, 6H, $\underline{CH_2}$), 2.10 (s, 3H, Ar$\underline{CH_3}$), 2.20 (s, 3H, Ar$\underline{CH_3}$), 3.40 (br, 4H, N$\underline{CH_2}$)

Compound 45

^{1}H N.M.R. δ(ppm) 1.20 (t, 3H, $CH_2\underline{CH_3}$), 2.10 (s, 3H, Ar$\underline{CH_3}$), 2.20 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 3H, N$\underline{CH_3}$), 3.40 (br, 2H, N$\underline{CH_2}$)

Compound 50

^{1}H N.M.R. δ(ppm) 2.10 (s, 3H, Ar$\underline{CH_3}$), 2.20 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 6H, N($\underline{CH_3}$)$_2$)

Compound 51

^{1}H N.M.R. δ(ppm) 2.10 (s, 3H, Ar$\underline{CH_3}$), 2.20 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 6H, N($\underline{CH_3}$)$_2$)

Compound 52

^{1}H N.M.R. δ(ppm) 2.18 (s, 6H, Ar$\underline{CH_3}$), 2.98 (s, 6H, Ar$\underline{CH_3}$)

Compound 53

^{1}H N.M.R. δ(ppm) 2.00 (s, 3H, Ar$\underline{CH_3}$), 2.20 (s, 3H, Ar$\underline{CH_3}$), 3.00 (s, 6H, (N$\underline{CH_3}$)$_2$)

N,N-Dimethyl-*N'*-[3-(3-trifluoromethylphenoxy)-2-tolyl]formamidine

Compound 54

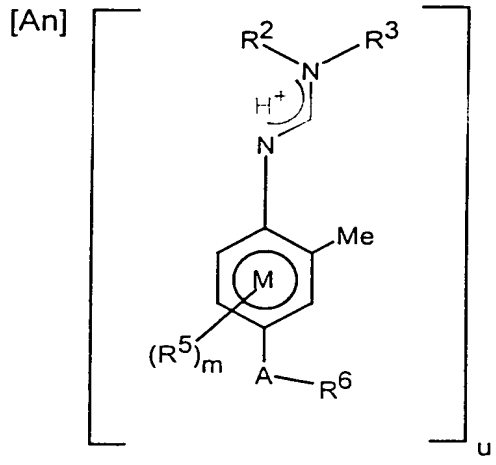
Was prepared using methods analogous to those described hereinabove, ^1H N.M.R. δ(ppm) 2.10 (s, 3H, $ArCH_3$), 3.00 (s, 6H, $N(CH_3)_2$)

Example 9

N,N-Dimethyl-*N'*-[4-(3-trifluoromethylphenoxy)-2,5-xylyl]formamidine sulfate salt (Compound 102)

To a solution of the compound 1 (see Table 1) (0.3g) in ethanol (0.3 ml) was added dropwise concentrated sulfuric acid (0.098 g). The mixture was filtered and the resulting solid was washed with diethyl ether to give the title compound as a solid, m.p. 178-80 °C.

The following compounds of formula X (see Table 2), i.e. salts of general formula I where -A-R^6 is para to the amidine moiety, R^1 is hydrogen, R^4 is methyl, An is an anion and u is 1 or 2 depending on the valency of the anion, may be prepared by methods analogous to Examples 9.



(X)

Table 2

Cmp	R^2	R^3	$(R^5)_m$	A	R^6	An^-	m.p./°C
100	Me	Me	5-Me	$-OCH_2-$	3-CF_3-phenyl	sulfate	215-7
101	Me	Me	5-Me,6-Br	O	3-CF_3-phenyl	sulfate	114-8

102	Me	Me	5-Me	O	3-CF_3-phenyl	sulfate	178-80
103	Me	Me	5-Me	O	3-CF_3-phenyl	chloride	152-4
104	Me	Me	5-Me	O	3-CF_3-phenyl	*p*-toluenesulfonate	133-5
105	Me	Me	5-Me	O	3-CF_3-phenyl	saccharinate	oil
106	Me	Me	5-Me	O	3-CF_3-phenyl	trifluoroacetate	141-3
107	Me	Me	5-Me	O	3-CF_3-phenyl	methanesulfonate	151-3
108	Me	Me	5-Me	O	3-CF_3-phenyl	oxalate	184-6
109	Me	Me	5-Me	O	3-CF_3-phenyl	camphorsulfonate	oil
110	-$(CH_2)_4$-		5-Me	O	3-CF_3-phenyl	chloride	159-63

Those compounds in the above table which do not have discrete melting points have the following characteristic ^{1}H N.M.R. data in $CDCl_3$.

Compound 105

^{1}H N.M.R. δ(ppm) 2.15 (s, 3H, Ar$\underline{CH_3}$), 2.25 (s, 3H, Ar$\underline{CH_3}$), 3.20 (s, 3H, N($\underline{CH_3}$)), 3.25 (s, 3H, N($\underline{CH_3}$)), 10.20-10.80 (br, 1H, NH)

Compound 109

^{1}H N.M.R. δ(ppm) 0.75 (s, 3H, C$\underline{CH_3}$), 1.05 (s, 3H, C$\underline{CH_3}$), 1.25 (d, 2H, $\underline{CH_2}$), 1.75-1.95 (m, 3H), 2.15 (s, 3H, Ar$\underline{CH_3}$), 2.20 (m, 1H, $\underline{CH}$), 2.25 (s, 3H, Ar$\underline{CH_3}$), 2.35 (d, 1H, $\underline{CH}$), 2.60 (t, 1H, $\underline{CH}$), 2.85 (d, 1H, $\underline{CH}$), 3.20 (s, 3H, N($\underline{CH_3}$), 3.30 (s, 3H, N($\underline{CH_3}$).

Test Example

Compounds were assessed for activity against one or more of the following:

Phytophthora infestans: late tomato blight

Erysiphe graminis f. sp. tritici: wheat powdery mildew

Pyricularia oryzae: rice blast

Leptosphaeria nodorum: glume blotch

Aqueous solutions or dispersions of the compounds at the desired concentration, including a wetting agent, were applied by spray or by drenching the stem base of the test plants, as appropriate. After a given time, plants or plant parts were inoculated with appropriate test pathogens before or after application of the compounds as appropriate, and kept under controlled environmental conditions suitable for maintaining plant growth and development of the disease. After an appropriate time, the degree of infection of the affected part of the plant was visually estimated. Compounds are assessed on a score of 1 to 3 where 1 is little or no control, 2 is moderate control and 3 is good to total control. At a concentration of 500 ppm (w/v) or less, the following compounds scored 2 or more against the fungi specified.

Phytophthora infestans

7, 8, 28, 30 and 46.

Erysiphe graminis f. sp. tritici:

1, 3, 4, 5, 7, 8, 9, 11, 12, 13, 15, 16, 17, 18, 19, 20, 21, 22, 23, 35, 37, 38, 39, 40, 41, 43, 45, 48, 49, 50, 100 and 110.

Pyricularia oryzae

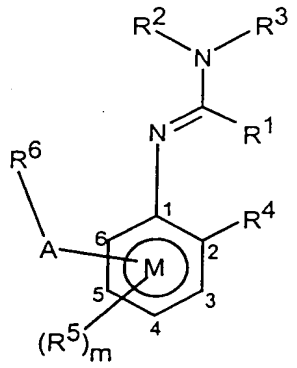
7, 17, 21, 23, 38, 41, 43, 45 and 100.

Leptosphaeria nodorum

1, 2, 5, 7, 8, 15, 17, 35, 37, 41, 43, 45 and 48.

Claims

1 The use of a compound of general formula I and salts thereof as fungicides



(I)

wherein

R^1 is alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl, each of which may be substituted, or hydrogen;

R^2 and R^3, which may be the same or different, are any group defined for R^1; cyano; acyl; $-OR^a$ or $-SR^a$, where R^a is alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl, each of which may be substituted; or R^2 and R^3, or R^2 and R^1, together with their interconnecting atoms may form a ring, which may be substituted;

R^4 is alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl, each of which may be substituted; hydroxy; mercapto; azido; nitro; halogen; cyano; acyl; optionally substituted amino; cyanato; thiocyanato; $-SF_5$; $-OR^a$; $-SR^a$ or $-Si(R^a)_3$;

m is 0 to 3;

when present R^5, which may be the same or different to any other R^5, is any group defined for R^4;

R^6 is optionally substituted carbo- or heterocyclyl; and

A is a direct bond, $-O-$, $-S(O)_n-$, $-NR^9-$, $-CR^7=CR^7-$, $-C\equiv C-$, $-A^1-$, $-A^1-A^1-$, $-A^3-$, $-A^4-$, $-A^1O-$, $-A^1S(O)_n-$, $-OA^1-$, $-S(O)_nA^1-$, $-A^1-A^4-$, $-A^1-A^4-C(R^8)=N-N=CR^8-$, $-A^1-A^4-C(R^8)=N-X^2-X^3-$, $-A^1-A^4-A^3-$, $-A^1-A^4-N(R^9)-$, $-A^1-A^4-X-CH_2-$, $-A^1-A^4-A^1-$, $-A^1-A^4-CH_2X-$, $-A^1-A^4-C(R^8)=N-X^2-X^3-X^1-$, $-A^1-X-C(R^8)=N-$,

$-A^1-X-C(R^8)=N-N=CR^8-$, $-A^1-X-C(R^8)=N-N(R^9)-$, $-A^1-X-A^-X^1-$,
$-A^1-O-A^3-$, $-A^1-O-C(R^7)=C(R^8)-$, $-A^1-O-N(R^9)-A^2-N(R^9)-$,
$-A^1-O-N(R^9)-A^2-$, $-A^1-N(R^9)-A^2-N(R^9)-$, $-A^1-N(R^9)-A^2-$,
$-A^1-N(R^9)-N=C(R^8)-$, $-A^3-A^1-$, $-A^4-A^3-$, $-A^2-NR^9-$, $-A^1-A^2-X^1-$,
$-A^1-A^1-A^2-X^1-$, $-O-A^2-N(R^9)-A^2-$, $-CR^7=CR^7-A^2-X^1-$,
$-C\equiv C-A^2-X^1-$, $-N=C(R^8)-A^2-X^1-$, $-C(R^8)=N-N=C(R^8)-$,
$-C(R^8)=N-N(R^9)-$, $-(CH_2)_2-O-N=C(R^8)-$ or $-X-A^2-N(R^9)-$

where

n is 0, 1 or 2,

A^1 is $-CHR^7-$,

A^2 is $-C(=X)-$,

A^3 is $-C(R^8)=N-O-$,

A^4 is $-O-N=C(R^8)-$,

X is O or S;

X^1 is O, S, NR^9 or a direct bond,

X^2 is O, NR^9 or a direct bond,

X^3 is hydrogen, $-C(=O)-$, $-SO_2-$ or a direct bond,

R^7, which may be the same or different to any other R^7, is optionally substituted alkyl, cycloalkyl or phenyl, each of which may be optionally substituted, hydrogen, halogen or cyano;

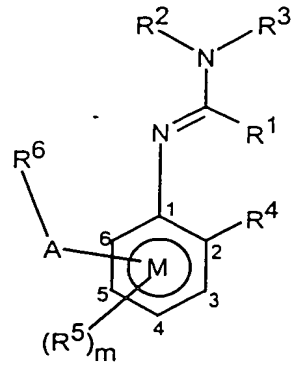
R^8, which may be the same or different to any other R^8, is alkyl, alkenyl, alkynyl, alkoxy, alkylthio, each of which may be optionally substituted, carbo- or heterocyclyl which may be optionally substituted, or hydrogen;

R^9, which may be the same or different to any other R^9, is optionally substituted alkyl, optionally substituted carbo- or heterocyclyl, or is hydrogen or acyl; or two R^9 groups on A, together with the connecting atoms, form a 5 to 7 membered ring;

where the moiety depicted on the right side of linkage A is attached to R^6;

or $-A-R^6$ and R^5 together with benzene ring M form an optionally substituted fused ring system.

2 A compound of formula I



(I)

wherein

R^1 is alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl, each of which may be substituted, or hydrogen;

R^2 and R^3, which may be the same or different, are any group defined for R^1, or together with the nitrogen to which they are attached may form a ring, which may be substituted;

R^4 is alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl, each of which may be substituted;

m is 1;

R^5 is any group defined for R^4 attached to the 5-position of the benzene ring M;

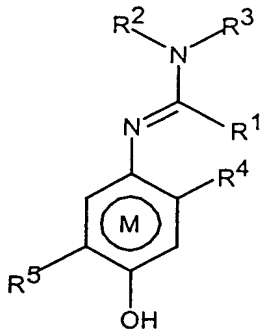
R^6 is optionally substituted carbo- or heterocyclyl; and

A is a direct bond; –O-; -S-; $-NR^9-$, where R^9 is alkyl, alkenyl, or alkynyl, each of which may be substituted by alkoxy, haloalkoxy, alkylthio, halogen or optionally substituted phenyl; $-CHR^7-$ or $-O-CHR^7-$, where R^7 is alkyl, alkenyl, or alkynyl, which may be substituted by alkoxy, haloalkoxy, alkylthio, halogen or optionally substituted phenyl; hydroxy; halogen; cyano; acyl; alkoxy; haloalkoxy; or alkylthio;

where $-A-R^6$ is in the 4-position of the benzene ring M and the moiety depicted on the right side of linkage A is attached to R^6;

or –A-R^6 and R^5 together with benzene ring M form an optionally substituted fused ring system.

3 A compound of general formula IXa,



(IXa)

where

R^1 is alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl, each of which may be substituted, or hydrogen;

R^2 and R^3, which may be the same or different, are any group defined for R^1; cyano; acyl; -OR^a or -SR^a, where R^a is alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl, each of which may be substituted; or R^2 and R^3, or R^2 and R^1, together with their interconnecting atoms may form a ring, which may be substituted;

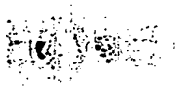
R^4 is alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl, each of which may be substituted; and

R^5 is any group defined for R^4;

with the proviso that R^5 is not tert-butyl.

4 A pesticidal composition comprising at least one compound as claimed in claim 1 in admixture with an agriculturally acceptable diluent or carrier.

5 A method of combating pests at a locus infested or liable to be infested therewith, which comprises applying to the locus a compound as claimed in claim 1.



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